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Translation of "Stroyeniye diagrammy sostoyaniya sistemy titan-med'"
Poroshkovaya Metallurgiya,
No. 6(42), pp. 77-87, June 1966

FACILIT' FORM 602

N67 18925

(ACCESSION NUMBER)

14

(PAGES)

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

17

(CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON

JANUARY 1967

PHASE-DIAGRAM STRUCTURE OF THE TITANIUM-COPPER SYSTEM

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The phase diagrams of the titanium-copper system were studied by metallographic, thermographic, X-ray and microhardness analyses at concentrations of 20 to 100 at. percent Cu. The results and the data in the literature enabled the authors to construct a phase diagram of the Ti-Cu system. In this system, six metallides exist, of which Ti_2Cu , $TiCu$

and $TiCu_4$ form phases of variable composition with narrow regions of homogeneity.

Investigation of the titanium-copper phase diagram was started as early /77* as the 30's. A great deal of information is given in the literature on research into this system. In some papers copper- or titanium-rich sections of the diagram were studied (refs. 1, 2, 4 and 10-14), or the structure of one or two intermetallic phases was investigated (refs. 3, 6, 15, 16). In others (research by Karlsson, 1951 (ref. 5), Raub et al., 1952 (ref. 7), Joukainen et al., 1952 (ref. 8) and Trzebiatowski et al., 1953 (ref. 9)) the phase diagram was studied over a wide range of concentrations. In comparing these works, attention is drawn to the ambiguity of the given results. There is no unanimous opinion on the number of intermetallic phases formed in the system, the regions of temperature and concentration in which they exist, the type of melting, or the crystal structure. The reason for this discrepancy is the effect of impurities contained in the initial materials and contaminating the alloys during melting and heat treatment. This applies particularly to the first papers devoted to investigation of the phase diagram. Some research workers interpret their results incorrectly. Reliable data may be obtained only by eliminating the effect of impurities and using various methods of physicochemical analysis for studying the structure of the phase diagram.

We used the metallographic, thermographic, X-ray and microhardness methods of analysis for studying the phase diagram of the titanium-copper system in the range from 20 to 100 at. percent concentration of copper. All available information in the literature on the titanium-copper system was taken into consideration in analyzing the resultant data.

The initial materials were titanium iodide (TU 8029-59) with the following impurity content (in percent): Fe, 0.015; Mg, 0.01; Mn, 0.005; Ni, 0.01; Cr, 0.01; Al, 0.02; Si, 0.01; C, 0.015; O_2 , 0.02; N_2 , 0.02; and electrolytic copper

grade V3 (TU 704-59) with the following impurity content (in percent): $Bi < 2 \cdot 10^{-4}$, $Fe < 2 \cdot 10^{-4}$, $Mg < 3 \cdot 10^{-4}$, $Mn < 2 \cdot 10^{-4}$, $As < 2 \cdot 10^{-4}$, $Ni < 3 \cdot 10^{-4}$, $Sn < 2 \cdot 10^{-4}$, $Pb < 2 \cdot 10^{-4}$, $Sb < 3 \cdot 10^{-4}$, $Zn < 3 \cdot 10^{-4}$, $Si < 3 \cdot 10^{-4}$.

*Numbers given in margin indicate pagination in original foreign text.

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The alloys were melted in an arc furnace with a permanent tungsten electrode on a water-cooled copper hearth in a pure argon atmosphere. The argon was additionally purified by melting pure titanium as a getter for several minutes. The ingots were turned over and melted twice to produce uniform alloys. After melting, the ingots were teemed into massive copper molds in the same furnace. The alloys were homogenized by annealing in evacuated quartz ampules. The specimens were placed in molybdenum containers to prevent contact with the quartz. The alloys were annealed at 800°C for 300 hr. Alloys quenched from various temperatures in ice water were also studied to determine the regions of phase homogeneity. Prehomogenized alloys were held at the quenching temperatures for 1-2 hr. Chemical analysis was used for checking the composition of the alloys, and it was found that deviation from the charge composition was less than 0.5 at. percent in most cases. Alloy compositions are therefore given with respect to the charge. /78

The following etchants were used for microstructural analysis of the alloys: a mixture of various quantities of 3 percent hydrogen peroxide and 25 percent ammonia was used for copper-rich alloys (up to 25 at. percent Ti); the remaining alloys were electrolytically etched by a mixture of 40 percent HF (one part), HNO₃ with a specific gravity of 1.4 (one part) and glycerin (two parts).

The microhardness of the phases was measured on the PMT-3 instrument under loads of 20 and 50 grams. Thermal analysis of the alloys was done in an atmosphere of pure helium in crucibles made from Al₂O₃ or stabilized ZrO₂. Platinum-platinorhodium thermocouples were used as the temperature pickups. The thermocouple junctions were enclosed in thin-walled quartz jackets. A Kurnakov pyrometer was used as the registration instrument. Both heating and cooling curves of the annealed alloys were taken.

Powder patterns taken in RKD and VRS cameras in copper emission with a nickel filter were used for X-ray phase analysis of the alloys. X-ray photographs of the quenched specimens were taken from the microsection in RKD and RKE cameras. The phase diagram shown in figure 1 was constructed from the resultant data. This figure shows that there are six intermetallic phases in the titanium-copper system. Data on these phases are given in tables 1, 2 and 3.

The phase based on the compound Ti₂Cu melts congruently at a temperature of 1015°C and forms two eutectics: one with a solid solution based on β-Ti at 1003°C and 31 at. percent Cu, and the other with a phase based on the compound TiCu at 960°C and 43 at. percent Cu (fig. 2, a-b). These results agree with the data of reference 9. It is unlikely that Ti₂Cu is formed by a peritectic reaction as assumed in reference 8.

Karlsson (ref. 5), basing his opinion only on the data of X-ray phase analysis, erroneously attributed a composition corresponding to the formula Ti₃Cu to the titanium-rich phase. According to our data, the region of homogeneity for this phase at 900°C and below lies between 30 and 33 at. percent Cu. This

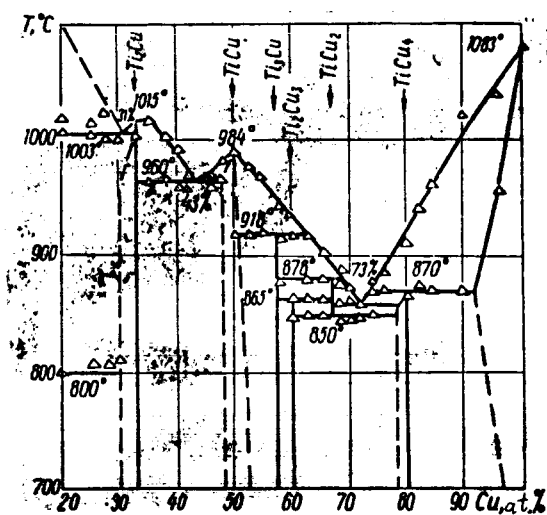


Figure 1. Phase diagram of the titanium-copper system.

is apparent from microstructural analysis of quenched alloys with 31 and 33 at. percent Cu (fig. 2, d-e). The alloy with 25 at. percent Cu obviously has a two-phase structure (fig. 2, f), while the line of eutectic transformation is registered on heating curves up to an alloy with 30 at. percent Cu. According to the data given by Laves (ref. 3) and Rostoker (ref. 6), this phase has a face-centered cubic lattice with 96 atoms per cell. Subsequent studies have revealed that the structure found in references 3 and 6 actually belongs to the triple oxide phase Ti_4Cu_2O resulting from oxygen contamination of the alloys. The true crystal structure of the phase based on the compound Ti_2Cu was identified by Mueller (ref. 15) as belonging to the type $MoSi_2$ (tetragonal lattice with six atoms per cell). This conclusion is confirmed by our studies (see table 1).

The phase based on the compound $TiCu$ melts congruently at a temperature of 984°C (at 975°C according to reference 8 and at 982°C according to reference 9) and has a region of homogeneity at 900°C and below in the interval from 48 to 52 at. percent Cu (fig. 2, g-j). According to the data of references 5 and 7, there are two phases based on the compound $TiCu$: a γ -phase with an excess of Ti which has a tetragonal lattice of the B11 type, and a δ -phase with an excess of Cu which has a tetragonal lattice of the CuAu type. There is actually only a single phase based on the compound $TiCu$ which has a tetragonal lattice of the B11 type with four atoms per cell (the γ -phase of references 5 and 7).

The phases based on compounds Ti_3Cu_4 and Ti_2Cu_3 have similar crystal structures. Most investigators have therefore assumed that they were a single phase (the δ -phase of references 5 and 7) based on the compound Ti_2Cu_3 according to references 8, 9 and 12. Schubert (ref. 16) was the first to point out the existence of a phase based on the compound Ti_3Cu_4 . According to our data, these phases exist close to their stoichiometric composition and are formed by peritectic reactions at the following temperatures: Ti_3Cu_4 at 918°C (at 920°C according to reference 16 and at 935°C according to reference 9); Ti_2Cu_3 at 865°C. These phases also differ with respect to microhardness.

The crystal structure of the Ti_3Cu_4 phase was determined by Schubert (ref. 16) as having a tetragonal cell with 14 atoms per cell of the characteristic

TABLE 1. COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE ANGLES OF REFLECTION AND INTENSITIES OF INTERMETALLIC PHASES.

hkl	sin ² θ		(C) P·I(θ)· F ²		hkl	sin ² θ		(C) P·I(θ)· F ²	
	(A)	(B)	(A)	(B)		(A)	(B)	(A)	(B)
(D) Ti ₂ Cu					111	1386	1384	(G)	5.8
002	—	0,0202	—	4.7	003	—	1527	—	0.7
101	—	0733	—	3.8	112	—	1893	—	0.2
004	—	0807	—	0.8	013	2134	2134	(H)	9.2
103	0,1143	1137	(E)	100	020	2428	2428	(F)	17.9
110	1371	1366	(F)	37.3	021	—	0,2598	—	2.1
112	—	1568	—	1.2	004	2722	2715	(H)	4.8
006	1840	1817	(F)	11.7	113	—	2741	—	1.9
105	—	9145	—	0.9	022	—	3107	—	0.1
114	—	2173	—	0.8	121	—	3205	—	0.1
200	2737	2732	(F)	11.2	014	—	3322	—	0.3
202	—	2934	—	0.5	122	3737	3714	(E)	30.4
107	—	3156	—	0.4	114	3937	3929	(F)	10.0
116	3202	3183	(F)	17.2	023	—	3955	—	0.5
008	—	3230	—	0.1	005	4247	4243	(G)	1.3
211	—	3465	—	0.7	123	4577	4562	—	5.1
204	—	3539	—	0.3	015	—	4850	—	1.7
213	3878	3869	(E)	23.9	220	4848	4856	(F)	5.6
206	4570	4549	(F)	9.5	221	—	5026	—	0.8
118	—	4596	—	0.2	024	5151	5143	(F)	6.9
215	—	4677	—	0.4	115	5462	5457	(H)	3.7
109	4816	4771	(F)	8.7	222	—	5535	—	0.05
0,010	—	5947	—	0.05	031	—	5633	—	0.02
220	5482	5464	(G)	3.8	124	—	5750	—	0.3
222	—	5666	—	0.2	130	6067	6070	(F)	9.1
217	—	5888	—	0.3	006	—	6110	—	0.1
208	—	5962	—	0.2	032	6167	6142	(F)	8.2
301	—	6197	—	0.2	131	—	6240	—	1.3
224	—	6271	—	0.2	223	—	6383	—	0.3
1,1,10	—	6413	—	0.2	025	—	6671	—	3.4
303	6628	6601	(H)	6.9	016	6711	6717	(F)	3.1
0,1,11	—	6790	—	0.2	132	—	6749	—	0.1
310	0,6849	0,6830	(H)	7.0	033	—	6990	—	2.0
312	—	7032	—	0.3	125	7305	7278	(G)	2.8
0,012	7310 _{a1}	7268	(H)	18.0	116	—	7324	—	0.3
226	—	7281	—	7.2	224	7585	7571	(F)	6.4
305	—	7408	—	0.2	133	—	7597	—	0.7
219	7559 _{a1}	7503	(F)	15.0	231	—	8061	—	0.03
314	—	7637	—	0.4	034	—	8178	—	0.2
2,0,10	—	7779	—	0.2	007	—	8316	—	0.9
307	—	8620	—	0.2	026	—	8538	—	0.3
1,1,12	—	8634	—	9.8	232	8581 _{a1}	8570	(E)	22.5
316	8688 _{a1}	8647	(F)	19.5	134	8787 _{a1}	8785	—	17.5
228	—	8694	—	0.2	017	8957 _{a1}	8923	(F)	6.9
321	—	8929	—	0.5	225	—	9099	—	5.6
0,1,13	—	9213	—	0.3	126	9137 _{a1}	9145	(E)	11.0
323	9370 _{a1}	9333	(F)	28.4	233	—	0,9418	—	7.9
2,1,11	—	9522	—	0.7	117	9518 _{a1}	9530	(H)	6.9
0,0,14	—	9893	—	0.2	035	—	9706	—	4.4
(D) TiCu					040	—	9712	—	13.8
001	—	0,0170	—	22.8	041	—	9882	—	2.7
002	—	0679	—	0.2	(D) Ti ₂ Cu ₄				
011	—	0777	—	0.1	002	—	0,0059	—	15.0
110	0,1219	1214	(E)	59.2	004	—	0238	—	0.7
012	1288	1286	(E)	100	006	—	0536	—	25.3
					011	—	0619	—	0.1

Note: A, observed; B, calculated; C, intensity; D, phase; E, strong; F, moderate; G, very weak; H, weak; I, very strong.

TABLE 1. (CONTINUED).

hkl	sin ² θ		(C) P · I(0) · F ²		hkl	sin ² θ		(C) P · I(0) · F ²	
	(A)	(B)	(A)	(B)		(A)	(B)	(A)	(B)
013	—	0739	—	2,5	0.2.18	—	7244	—	0,03
008	—	0953	—	0,3	2.1.17	—	7327	—	3,7
015	—	0977	—	1,9	3.1.10	—	7534	—	1,8
110	0,1210	1209	(E)	67,6	2.2.14	7769	7755	(F)	7,2
112	1264	1268	(H)	1,4	321	—	7873	—	0,01
017	1340	1334	(I)	100	3.0.13	—	7958	—	0,9
114	1489	1447	(F)	2,7	323	—	7992	—	0,2
116	—	1745	—	1,3	3.1.12	—	8190	—	1,4
019	1813	1811	(H)	7,4	325	—	8231	—	0,2
0.0.12	—	2145	—	0,7	0.2.20	—	8376	—	1,8
118	—	2162	—	0,3	2.1.19	—	8399	—	2,0
0.1.11	—	2407	—	1,0	1.1.22	—	0,8418	—	0,3
0.20	2418	2418	(E)	20,6	0.1.23	—	8484	—	4,8
022	—	2478	—	0,5	0.024	—	8579	—	0,6
024	—	2656	—	1,0	327	8584α ₁	8588	(E)	22,6
1.1.10	—	2698	—	0,2	2.2.16	—	8649	—	3,7
0.0.14	2926	2919	(H)	2,3	3.0.15	—	8792	—	5,5
026	—	2954	—	0,5	3.1.14	8962α ₁	8964	(E)	20,6
0.1.13	—	3122	—	1,9	329	—	9065	—	1,0
1.1.12	—	3354	—	1,3	2.1.21	9590α ₁	9591	(F)	20,9
028	—	3371	—	0,1	0.2.22	—	9627	—	0,6
127	3759	3752	(I)	33,4	2.2.18	—	9662	—	0,3
0.0.16	—	3813	—	1,2	3.2.11	—	9661	—	0,2
0.2.10	—	3907	—	0,1	—	—	9672	—	13,1
0.1.15	—	3956	—	0,006	402	—	9732	—	3,3
1.1.14	4137	4128	(F)	10,0	1.1.24	—	9788	—	11,4
129	4235	4229	(G)	3,5	3.1.16	—	9858	—	8,4
0.2.12	—	4563	—	0,8	404	—	9910	—	0,4
2.1.11	—	4825	—	0,7	0.1.25	—	9914	—	30,1
0.0.18	—	4826	—	0,01					
220	0,4834	0,4836	(F)	6,5					
222	—	4896	—	0,2					
0.1.17	—	4909	—	0,03	002	—	0,0122	—	1,1
1.1.16	5035	5022	(F)	3,2	004	—	0486	—	1,7
224	—	5074	—	0,4	101	—	0633	—	4,7
0.2.14	5350	5337	(F)	7,2	103	—	0876	—	0,4
226	—	5372	—	0,1	006	—	1094	—	0,5
301	—	5455	—	0,005	110	0,1221	1206	(E)	61,2
1.2.13	—	5540	—	1,7	112	—	1327	—	0,02
303	—	5574	—	0,1	—	1351	1363	(E)	100,0
228	—	5789	—	0,4	—	1696	1692	(G)	1,1
305	—	5813	—	0,1	008	—	1945	—	0,03
0.0.20	—	5958	—	0,4	107	—	2092	—	0,1
0.1.19	—	5981	—	0,8	016	—	2300	—	2,6
1.1.18	—	6035	—	0,03	200	2436	2412	(E)	18,9
310	6053	6045	(F)	10,6	202	—	2533	—	0,1
312	—	6105	—	0,3	204	—	2898	—	0,5
0.2.10	6180	6170	(F)	9,3	0.0.10	0,3092	3039	(G)	6,3
314	—	6231	—	2,7	211	—	3045	—	0,9
2.2.10	—	6283	—	0,6	109	—	0,3065	—	0,4
2.1.15	—	6325	—	0,05	118	—	3151	—	0,06
316	—	6374	—	0,01	213	—	3288	—	0,1
309	—	6581	—	0,3	206	—	3506	—	0,3
2.2.12	—	6647	—	1,2	215	3793	3775	(E)	34,3
318	—	6981	—	0,6	1.1.10	4252	4245	(H)	15,6
1.1.20	—	6988	—	0,8	0.1.11	—	4280	—	0,3
0.1.21	—	7167	—	1,5	208	—	4357	—	0,04
0.0.22	—	7173	—	3,6	0.012	—	4376	—	0,01
3.0.11	—	7209	—	0,1	217	—	4504	—	0,1
	—	7243	—	0,3	220	4864	4824	(H)	6,0

TABLE 1. (CONCLUDED).

hkl		sin² θ		(C) P · f(θ) · F²		hkl		sin² θ		(C) P · f(θ) · F²	
		(A)	(B)	(A)	(B)			(A)	(B)	(A)	(B)
222	—	4945	—	0,03	033	3507	3514	(H)			
224	—	5310	—	0,2	133	3788	3826	(E)			
2.0.10	5464	5451	(G)	10,3	331	3903	3942	(F)			
301	—	5457	—	0,2	340	4267	4292	(G)			
219	—	5477	—	0,4	260	4559	4596	(H)			
1.1.12	—	5582	—	0,03	004	4709	4752	(F)			
303	—	5700	—	0,03	104	5026	5064	(H)			
0.1.13	—	5739	—	0,03	262	5775	5784	(F)			
226	—	5918	—	0,2	271	6108	6122	"			
0.014	—	5957	—	0,05	180	6247	6290	"			
310	6046	6030	(H)	9,7	182	7447	7478	(H)			
312	—	6151	—	0,1	244	7447	7488	(H)			
305	6192	6187	(H)	9,6	035	8250	8266	(E)			
314	—	6516	—	0,3	135	8563	8574	(H)			
2.1.11	—	6692	—	0,2	380	8772	8786	(F)			
228	—	6769	—	0,03	344	9031	9048	(G)			
2.0.12	—	6788	—	0,03	264	9338	9348	(H)			
307	—	6916	—	0,03							
316	—	7124	—	0,3							
1.1.14	—	7163	—	0,2							
0.1.15	—	7441	—	12,6	510	0,1166	0,1166	(G)			
0.0.16	—	7780	—	0,05	501	1183	1190	(H)			
2.2.10	7866α₁	7863	(G)	10,9	002	1266	1261	(E)			
321	—	7869	—	0,4	021	1480	1479	(F)			
309	—	7889	—	0,2	511	1500	1481	(E)			
318	—	7975	—	0,06	512	2439	2427	(E)			
323	—	8112	—	0,06	403	3391	3413	(H)			
2.1.13	—	8151	—	0,06	530	3503	3494	"			
2.0.14	—	8369	—	0,2	513	4016	4003	(F)			
325	8595α₁	8599	(G)	2,6	040	4659	4656	(G)			
1.1.16	—	8986	—	0,3	532	4759	4755	(F)			
3.1.10	0,9050α₁	9069	(G)	31,6	10,0.2	4813	4836	(H)			
3.0.11	—	9104	—	0,3	041	4970	4971	(F)			
2.2.12	—	9200	—	0,04	10,2.1	5041	5054	(H)			
327	—	9328	—	0,1	041	4970	4971	(F)			
0.1.17	—	9386	—	0,05	10,2.1	5041	5054	(H)			
400	—	9648	—	12,9	10,2.2	5994	6000	(G)			
402	—	9769	—	0,1	514	6220	6209	"			
0.018	—	9847	—	0,02	043	7475α₁	7493	"			
2.1.15	—	9853	—	80,7	10,2.3	7543α₁	7576	"			
					551	8448α₁	8440	"			
					534	8536α₁	8534	(H)			
					10,0.4	8599α₁	8618	"			
					025	9025α₁	9039	"			
					515	9044α₁	9041	"			
					552	9390α₁	9386	(G)			
					044	9708α₁	9699	"			
(D) TiCu₃											
002	0,1198	0,1188	(F)								
200	1238	1248	"								
131	1446	1446	"								
202	2439	2436	(E)								

type, which is confirmed by our data (see table 1). The Ti_2Cu_3 phase, according to our data, has a tetragonal lattice with 10 atoms per cell (type Os_2Al_3).

Schubert is mistaken in assuming that the Ti_2Cu_3 phase has a D_{4h}^7 space group

since the atomic coordinates in the elementary cell which he gives do not agree with this space group.

TABLE 2. CRYSTAL STRUCTURE OF THE INTERMETALLIC PHASES IN THE Ti-Cu SYSTEM.

(A)	(B)	(C)	(D)	(E) A	(F)	(G)		(J)
						(H)	(I)	
Ti ₃ Cu	MoSi ₃	(K)	$D_{4h}^{17}-I4/mmm$	$a=2,943$ $c=10,784$	6	5,64	5,69	2Cu (a): $(0, 0, 0);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ 4Ti (e): $(0, 0, z);$ $(0, 0, \bar{z}); (\frac{1}{2}, \frac{1}{2},$ $\frac{1}{2}+z); (\frac{1}{2}, \frac{1}{2},$ $\frac{1}{2}-z), z=0,341$
TiCu	TiCu	,	D_{4h}^7-P4/nmm	$a=3,107$ $c=5,919$	4	6,41	6,45	2Cu (c): $(0, \frac{1}{2},$ $z); (\frac{1}{2}, 0, \bar{z}),$ $z=0,10$ 2Ti (c): $(0, \frac{1}{2}, z);$ $(\frac{1}{2}, 0, \bar{z}); z=0,65$
Ti ₃ Cu ₄	Ti ₃ Cu ₄	,	$D_{4h}^{17}-I4/mmm$	$a=3,126$ $c=19,964$	14	6,78	6,69	4Cu (e): $(0, 0, z);$ $(0, 0, \bar{z});$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z),$ $z=0,13_5$ 4Cu (e): $(0, 0, z);$ $(0, 0, \bar{z});$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z),$ $z=0,43_0$ 2Ti (a): $(0, 0, 0);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2});$ 4Ti (e): $(0, 0, z);$ $(0, 0, \bar{z});$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z),$ $z=0,29_5$

Note: A, phase; B, type; C, system; D, space group; E, lattice parameters; F, number of atoms per cell; G, density; H, calculated; I, measured; J, atomic coordinates; K, tetragonal; L, rhombic, M, undetermined.

TABLE 2. (CONCLUDED).

(A)	(B)	(C)	(D)	(E) A	(F)	(G)		(J)
						(H)	(I)	
Ti ₃ Cu ₈	Os ₂ Al ₃	(K)	$D_{4h}^{17}-I4/mmm$	$a=3,140$ $c=13,962$	10	6,96	7,10	2Cu (a): (0, 0, 0); $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; 4Cu (e): (0, 0, z); (0, 0, $\bar{z}$); $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z)$; $z \sim 0,2$ 4Ti (e): (0, 0, z); (0, 0, $\bar{z}$); $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z)$; $z \sim 0,4$
TiCu ₂	VAu ₂	(L)	$C_{2v}^{14}-Amm2$	$a=4,363$ $b=7,977$ $c=4,478$	12	7,41	7,16	
TiCu ₄	TiCu ₄	,	(M)	$a=12,897$ $b=4,522$ $c=4,344$	20	7,88	7,81	

TABLE 3. SOME CHARACTERISTICS OF INTERMETALLIC PHASES IN THE Ti-Cu SYSTEM.

Phase	Region of homogeneity at 800°C, at.% Cu	Temperature region of existence, °C	Type of melting	Hardness, daN/mm ²
Ti ₂ Cu	30-33	1,015 and below	Congruent	442±14
TiCu	48-52	984 and below	Congruent	553±25
Ti ₃ Cu ₄	57	918 and below	Incongruent	500±15
Ti ₂ Cu ₃	60	865 and below	Decomposes into two solid phases	597±5
TiCu ₂	--	878-850	Incongruent	253±34
TiCu ₃	78-80	870 and below	Incongruent	504±5

The TiCu_2 phase, which exists only at high temperatures, was observed in references 9 and 16. According to our data, this phase exists in a narrow temperature region from 878° to 850°C (from 892° to 872°C according to reference 9). At 850°C , TiCu_2 decomposes into Ti_2Cu_3 and TiCu_4 . Figure 2, j-k, shows the microstructure of the alloy with 66 at. percent Cu in the cast state and after annealing at 800°C . The crystal structure of the TiCu_2 phase was determined by Schubert (ref. 16) as having a rhombic lattice with 12 atoms per cell (type VAu_2) which is confirmed by our data (table 1). /85

The intermetallic phase richest in copper in the Ti-Cu system is formed by a peritectic reaction at 870°C and has a region of homogeneity in the interval from 78 to 80 at. percent Cu. Most authors attribute an ideal composition to this phase corresponding to the formula TiCu_3 , although a region of homogeneity /86 with a higher copper concentration than the TiCu_3 composition is indicated.

Zwicker (ref. 13) attributes an ideal composition to this phase corresponding to the formula Ti_2Cu_7 (78 at. percent Cu). A microstructural comparison of alloys

with 80 and 75 at. percent Cu annealed at 800°C (fig. 2, m) shows that the first has a single-phase structure while the second is a two-phase alloy. This impels us to give preference to the formula TiCu_4 for the compound based on this phase.

The X-ray pattern for this phase resolves into a rhombic lattice. The compound TiCu_4 should have an elementary cell with 20 atoms and a parameter a five times

as great as the TiCu_3 cell. The measured density for TiCu_4 agrees well with the density calculated from X-ray data. The space group for the phase based on TiCu_4 is undetermined. The eutectic $\text{TiCu}_4+\text{TiCu}_2$ is shown in figure 2, c.

Thus there are six intermetallic phases in the Ti-Cu system. Four of these have a tetragonal lattice while two have a rhombic lattice. The phases Ti_2Cu ,

Ti_3Cu_4 and Ti_2Cu_3 have the same substructure of the A6 (In) type and belong to the same space group with differences only in the order in which the layers of titanium and copper atoms alternate.

Conclusions

Alloys in the titanium-copper system are studied in the range of concentrations from 20 to 100 at. percent Cu by the methods of metallographic, thermographic, X-ray and microhardness analysis. The phase diagram for the Ti-Cu system is constructed on the basis of the resultant data together with information in the literature.

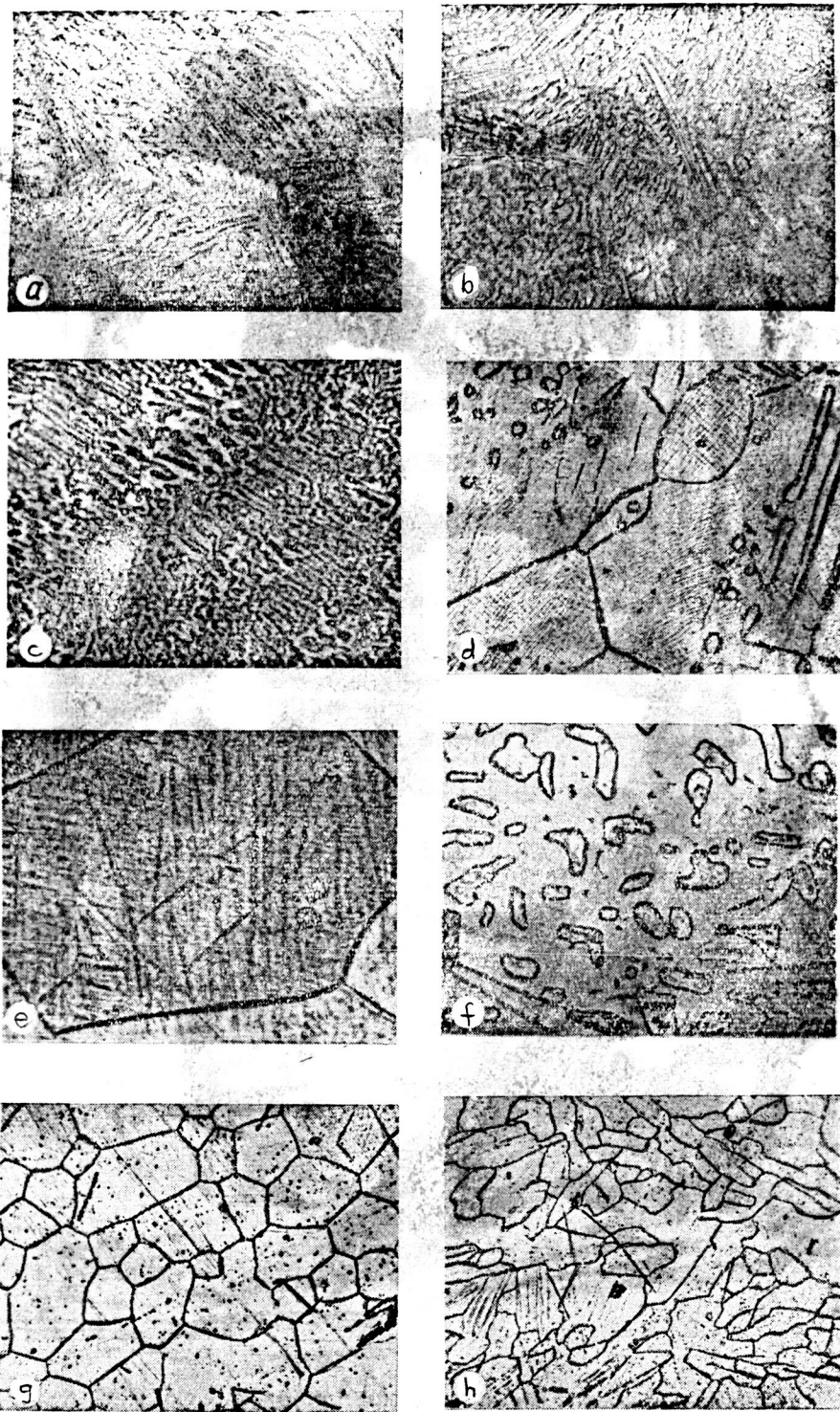
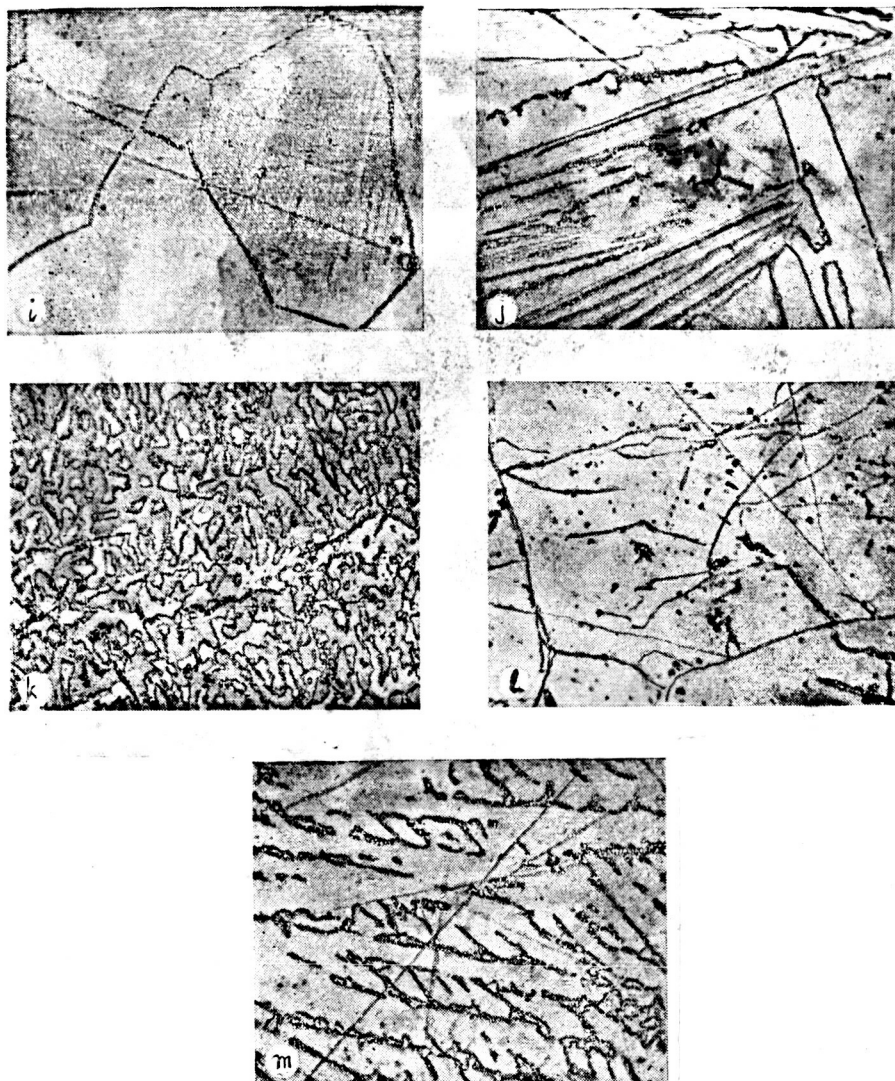


Figure 2. Microstructures of alloys in the titanium-copper system: a, alloy with 31 at. percent Cu, cast, eutectic $\text{Ti}_2\text{Cu}+\beta\text{-Ti}$, $\times 1440$; b, alloy with 43 at. percent Cu, cast, eutectic $\text{TiCu}+\text{Ti}_2\text{Cu}$, $\times 1440$; c, alloy with 73 at.

Figure 2, Continued



percent Cu, cast, eutectic $\text{TiCu}_4 + \text{TiCu}_2$, $\times 200$; d, alloy with 33 at. percent Cu, quenched from 900°C , phase Ti_2Cu and a small quantity of phase TiCu , $\times 270$; e, alloy with 31 at. percent Cu, quenched from 900°C , phase Ti_2Cu , $\times 350$; f, alloy with 25 at. percent Cu, annealed at 800°C for 300 hr, $\text{Ti}_2\text{Cu} + \alpha\text{-Ti}$, $\times 350$; g, alloy with 48 at. percent Cu, quenched from 900°C , phase TiCu , $\times 70$; h, alloy with 50 at. percent Cu, quenched from 930°C , phase TiCu , $\times 70$; i, alloy with 52 at. percent Cu, annealed at 800°C for 300 hr, phase TiCu , $\times 350$; j, alloy with 67 at. percent Cu, cast, phase TiCu_2 $\times 350$; k, alloy with 67 at. percent Cu, annealed at 800°C for 300 hr, $\text{TiCu}_4 + \text{Ti}_2\text{Cu}_3$, $\times 350$; l, alloy with 80 at. percent Cu, annealed at 800°C for 300 hr, phase TiCu_4 , $\times 350$; m, alloy with 75 at. percent Cu, annealed at 800°C for 300 hr, $\text{TiCu}_4 + \text{Ti}_2\text{Cu}_3$, $\times 350$.

It is shown that there are six intermetallic compounds in the system and that three of these, Ti_2Cu , TiCu and TiCu_4 form phases of variable composition with narrow regions of homogeneity.

The crystal structures of phases based on Ti_2Cu , TiCu , Ti_3Cu_4 and TiCu_2 are confirmed and the space group is determined for the phase based on Ti_2Cu_3 . It is shown that the formula TiCu_4 and a crystal lattice with a rhombic cell containing 20 atoms should be attributed to the intermediate phase richest in copper.

The compounds Ti_2Cu and TiCu melt congruently at 1015 and 984°C respectively, the compounds Ti_3Cu_4 , TiCu_2 and TiCu_4 are formed from the melt by peritectic reactions at 918°, 878° and 870°C respectively. TiCu_2 exists only at high temperatures and decomposes at 850°C into TiCu_4 and Ti_2Cu_3 . The compound Ti_2Cu_3 exists below 865°C and is formed at this temperature according to the reaction $\text{TiCu}_2 + \text{Ti}_3\text{Cu}_4 \rightarrow 2\text{Ti}_2\text{Cu}_3$ or at 850°C by decomposition of the compound TiCu_2 .

The coordinates of the three eutectics of the system are as follows: the eutectic between $\beta\text{-Ti}$ and Ti_2Cu lies at 1003°C and 31 at. percent Cu; the eutectic between Ti_2Cu and TiCu lies at 960°C and 43 at. percent Cu; and the eutectic between TiCu_2 and TiCu_4 lies at 860°C and 73 at. percent Cu.

Received 19 March 1966

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Translated for the National Aeronautics and Space Administration
by John F. Holman and Co. Inc.